Membrane and Water Treatment, *Vol. 13, No. 1 (2022) 1-6*
https://doi.org/10.12989/mwt.2022.13.1.001

Performance evaluation of nitrate removal in high TDS wet scrubber wastewater by ion exchange resin with dissolved air flotation (DAF) process

Bongchul Kim, Inseol Yeo and Chan-gyu Park*

Water Environment Center, Environmental Technology Division, Korea Testing Laboratory (KTL), 87, Disital-ro 26-gil, Guro-gu, Seoul, Republic of Korea

(Received May 14, 2021, Revised August 10, 2021, Accepted September 3, 2021)

Abstract. The regulations of the International Maritime Organization (IMO) have been steadily strengthened in ship emissions. Accordingly, there is a growing need for development of related technologies for the removal of contaminants that may occur during the treatment of SOx and NOx using a wet scrubber. However, this system also leads to wastewater production when the exhaust gas is scrubbed. In this research, we evaluated the performance of an ion selective resin process in accordance with scrubber wastewater discharge regulations, specifically nitrate discharge, by the IMO. Accelerated real and synthetic wastewater of wet scrubbers, contained high amounts of TDS with high nitrate, is used as feed water in lab scale systems. Furthermore, a pilot scale dissolved air flotation (DAF) using microbubble generator with ion exchange resin process was combined and developed in order to apply for the treatment of wet scrubber wastewater. The results of the present study revealed that operating conditions, such as resin property, bed volume (BV), and inlet wastewater flow rate, significantly affect the removal performance. Finally, through a pilot test, DAF with ion exchange resin process showed a noticeable improvement of the nitrate removal rate compared to the single DAF process.

Keywords: dissolved air flotation (DAF); international maritime organization (IMO) regulation; ion exchange resin; nitrate removal; wet scrubber wastewater treatment

1. Introduction

Reduction of air pollutant emissions plays a significant role in supporting sustainable development. Greenhouse gases (GHGs) are widely known to contribute to global warming (Fan *et al*. 2018, Isacs *et al*. 2016, Maucieri *et al*. 2017). Air contaminants such as Sulfur oxide (SOx), nitrogen oxide (NOx), volatile organic compounds (VOCs), and carbon monoxide (CO) have an immediate impact on human health and the environment. They also contribute to the formation of secondary contaminants such as particulate matter (PM) and ozone, which are among the leading causes of smog (Tan and Li 2000, Robichaud 2020, Rubio *et al* 2002).

Generally, transportation (27%) is the one of the main contributors to GHGs. On the basis of the Environmental Protection Department, maritime emissions for carriage of freight and passengers have remained relatively constant. The contaminants such as SOx, NOx, PM10, and PM2.5 by marine transport are the second biggest contributor. More specifically, shipping gave rise to emission portions of 39.72% SOx, 31.84% NOx, 48.08% PM10, and 95.74% PM2.5 from all European transportation (Van *et al*. 2109).

International Maritime Organization (IMO) regulations to reduce SOx emissions from ships first came into force in 2005, under Annex VI of the International Convention for the Prevention of Pollution from Ships, as known as the MARPOL convention. Since then, the limits on SOx have been continuously strengthened (Halff *et al*. 2019, Li *et al*. 2020, Lindstad and Eskeland 2016, Ni *et al*. 2020). From 1 January 2020, the limit for Sulfur in fuel oil used on board ships operating outside designated emission control areas has decreased to 0.5% m/m. This will considerably decrease the amount of SOx emitted from ships and should have major environmental and health benefits globally, especially for populations living close to coasts and ports (Halff *et al*. 2019, Li *et al*. 2020, Ni *et al*. 2020).

Many processes recently have been proposed and applied to comply with the regulations for emissions of ships. Remarkably, many companies including Wärtsilä Hamworthy Krystallon, DuPont BELCO Clean Air Technologies, Green Tech Marine, Alfa Laval Aalborg, and Marine Exhaust Solutions offer wet scrubber processes, because this system has smaller unit area and lower price than other technologies for installation on ships (Li *et al*. 2020, Panasiuk and Turkina 2015, Seddiek and Elgohary 2014, Yang *et al*. 2012). There are three wet scrubber types: an open loop type that uses seawater only; a closed loop type that uses fresh water with sodium hydroxide; and a hybrid type that offers both benefits. The type of open loop scrubber is to some extent a simple system and cheaper than the closed loop type (Lindstad and Eskeland 2016, Panasiuk and Turkina 2015, Kim and Seo 2019, Zhou and Wang 2020). On the other hand, this type cannot be operating in emission control areas (ECAs) (Li *et al*. 2020, Lindstad and Eskeland 2016, Ni *et al*. 2020).

All types of scrubbers, however, also lead to the production of wastewater during scrubbing of the exhaust

*Corresponding author, Ph.D.,
E-mail: pcg6189@naver.com

ISSN: 2005-8624 (Print), 2092-7037 (Online)

Table 1 Regulation of scrubber wash water discharge

Material	Unit	Discharge limit value
pH	-	6.5<
Turbidity	NTU	< 25
Nitrate	mg/L	< 60

Table 2 The limit of PAHs for various wastewater flow rates per MWh

Flow rate (m^3/MWh)	Discharge concentration limit (μg/L PAH_{phe} equivalents)
0 – 1	2250
2.5	900
5	450
11.25	200
22.5	100
45	50
90	25

Table 3 Chemical composition of the enriched raw and synthetic scrubber wastewater solution used for this research

Solution	Raw (mg/L)	Synthetic (mg/L)
Cl^-	266.917	269.44
NO_2^-	21	23.003
NO_3^-	551.27	558.05
SO_4^{2-}	5123.1	5283.3
Na^+	17890.13	2886.5
Mg^{2+}	4.71667	4.861
Ca^{2+}	23.0833	24.047

Table 4 Characteristics of ion exchange resins used for this research

Properties	Resin	
	A-62-MP	MIEX
Resin matrix	Cross linked polystyrene	Methacrylate, Macroporous
Functional group	Quaternary ammonium Type-1	Quaternary ammonium (trimethylamine functional group)
Ionic form	Chloride	Chloride
Appearance	Yellow to golden spherical beads	Brown, Opaque beads
T.E.C. meq/mL in Cl form	1	0.24 – 0.50
Particle size (mm)	0.3 - 1.2	0.18 – 0.25
Operational pH range	0 - 14	3 – 10

gas. This wastewater generally contains high TDS with various contaminants such as polyaromatic hydrocarbons (PAHs), suspended solids, and nitrate. For prevention of marine environment pollution, the IMO also regulates discharge water quality of scrubber wash water (Tables 1 and 2) (Li *et al*. 2020, Lindstad and Eskeland 2016, Ni *et al*. 2020).

Existing processes such as centrifugation and dissolve air flotation (DAF) are able to remove turbidity and PAHs (Salima *et al*. 2018, Younker and Walsh 2014). However, nitrate, an ionic pollutant, is not removed by these systems. Nitrate is a highly stable and soluble ion in aqueous solution. Thus, several processes have been used for nitrate removal, such as adsorption (Kamimura *et al*. 2017, Nekouei *et al*. 2019, Reinoso and Tonetto 2018, Soyluoglu *et al*. 2020), biological treatment (Rezvani *et al*, 2019, Lytle *et al*. 2007), and reverse osmosis (Epsztein *et al*. 2015). However, some of these systems have several drawbacks; for example, reverse osmosis has high operating costs with high TDS wastewater and biological treatment is not suitable for installation in ships.

In this research, we evaluated the performance of an ion selective resin process in accordance with scrubber wastewater discharge regulations, specifically nitrate, by the IMO. Various resin performance measures were assessed in batch and column tests to identify the best ion exchange resin for treatment of high TDS scrubber wastewater. The removal efficiency of nitrate was also evaluated for optimization of operating conditions. Based on the results, important operating conditions for improving the nitrate removal rate in ion exchange systems are delineated and discussed.

2. Materials and methods

2.1 Materials

Enriched synthetic scrubber wastewater was used for batch and column tests. The chemical composition of the synthetic scrubber wastewater was based on a real engine and scrubber system from A company pilot scrubber system, as summarized in Table 3. In order to accelerate scrubbing wastewater, a batch system of a pilot scrubber was operated for 12 hours. Specifically, to prepare an accelerated synthetic scrubbing wastewater, DI water was supplemented with 55.0 mM Na_2SO_4, 0.2 mM $MgSO_4$, 66.6 mM $CaCl_2$, 350.6 mM NaCl, 0.5 mM $NaNO_2$, and 9.0 mM $NaNO_3$.

2.2 Ion exchange resin

We used a microporous strongly basic anion exchange resin (Tulsion A 62 MP, Thermax, India) and a magnetic strong base anion exchange resin (MIEX, IXOM Watercare, Australia). These resin properties provided by the vendor are given in Table 4 (Du *et al*. 2019, Zhang *et al*. 2012, Zhou *et al*. 2012). Before use, all resins were rinsed with deionized water.

2.3 Batch test

Batch sorption experiments were conducted over different time periods from 0 min to 60 min. Fixed dosages (1 mL) of ion exchange resins were exposed to a set of 100 mL synthetic scrubber wastewater solution at 200 rpm and room temperature in a thermostat orbital shaker (SCILOGEX, SK-O330-Pro).

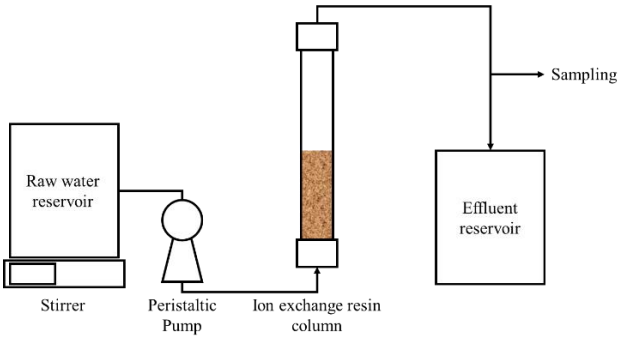
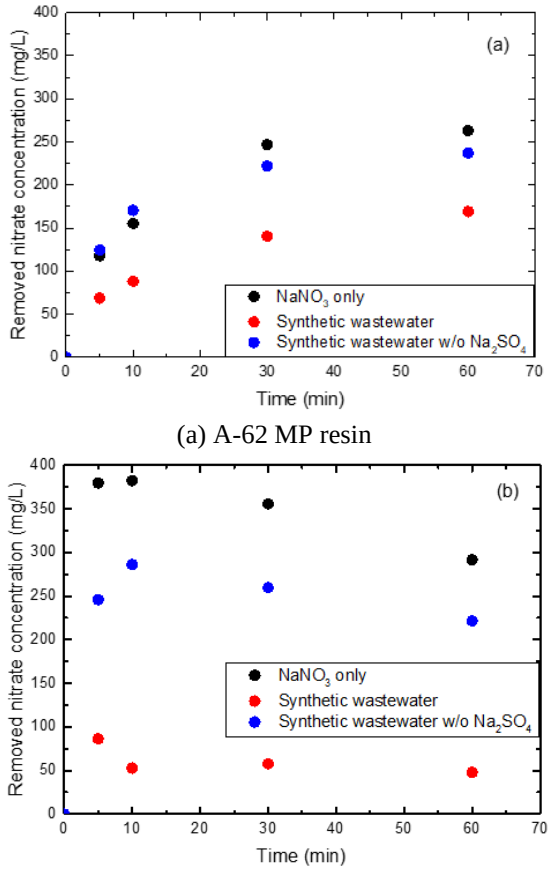


Fig. 1 Schematic illustration of ion exchange resin column test system



(a) A-62 MP resin

(b) MIEX resin

Fig. 2 Nitrate removal with various synthetic wastewater compositions by batch test of ion exchange resin

2.4 Column test

A schematic illustration of the ion exchange resin test system is shown in Fig. 1. The synthetic solution was passed through a column packed with the resins. The experiment was carried out at room temperature. Conditions of the column test were designed such that 21 and 35 mL of resin was packed inside a 50 mm diameter column. A peristaltic pump was used to pump the feed solution though the laboratory column.

2.5 Pilot test with dissolved air flotation (DAF) system

In order to apply for the treatment of wet scrubber wastewater, a pilot scale dissolved air flotation (DAF) using microbubble generator with ion exchange resin process was combined and developed. The processing capacity developed a system of 1 m^3/hr scale and trial run test for suggesting optimal operation was carried out under the following conditions. Initial concentrations of turbidity and nitrate were 150.50 ± 6.36 NTU and 113.34 ± 36.28 mg/L respectively. The amount of inorganic coagulant (PAC) injected was 100 mg/L. The flow rate was 10 LPM, and 30 L ion exchange resin, 50% bed volume, was used in this experiment. The experiment proceeded continuously operation for 1 hour.

3. Results and discussion

3.1 Batch test

Fig. 2 shows the nitrate removal with two different ion exchange resins. It was observed that nitrate removal was fast for the initial 30 minutes, as shown in Fig. 2.

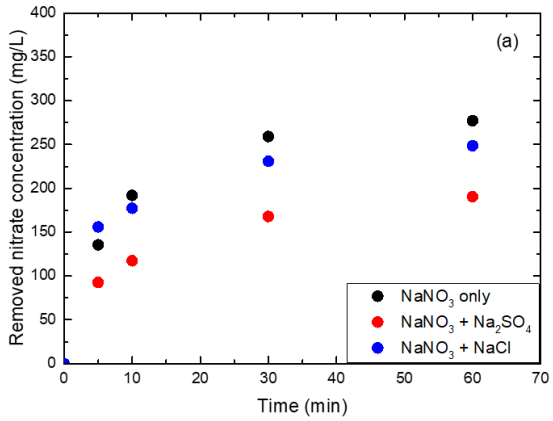
Experimental results showed higher nitrate removal by A-62 MP with synthetic wastewater. It is considered that the differences in the removal capacities of the resins arise from variation of the anion composition. To further understand the adsorption behavior, we verified the nitrate removal of these resins by anion compositions. As presented in Fig. 3, the adsorption rate with chloride + nitrate solution did not show a significant difference compared to the adsorption rate with the nitrate-only solution.

However, a substantial decline of the nitrate removal was observed when the sulfate + nitrate solution was employed. Interestingly, the nitrate removal declined significantly in the case of the MIEX resin with sulfated solution. As previously discussed, the selectivity of a general strongly alkaline resin, including MIEX, for the following ions is ordered as follows: $SO_4^{2-} > NO_3^- > Cl^- > F^- > HCO_3^-$; several nitrate selective resins, including A-62 MP, which have proven to have affinity for various ions, meanwhile follow the ranking $NO_3^- > SO_4^{2-} > Cl^- > HCO_3^-$ (Du *et al*. 2019). The carbon chain length of the quaternary ammonium groups is a significant factor of the ion exchange resin's nitrate selectivity, because the resin has larger electro-attraction to ions with larger charge and a smaller ionic diameter results in larger relative velocity (Nekouei *et al*. 2019, Reinoso and Tonetto 2018, Muhammad *et al*. 2019). Nitrate is better eliminating with steric strain than is sulfate due to an increase is carbon atoms and because the volume of the matrix of the resin occupies more space, causing an increase in steric strain. However, it also reduces the resin's exchange capacity, and therefore MIEX is more suitable for the treatment of low TDS raw water, especially at low sulfate concentration.

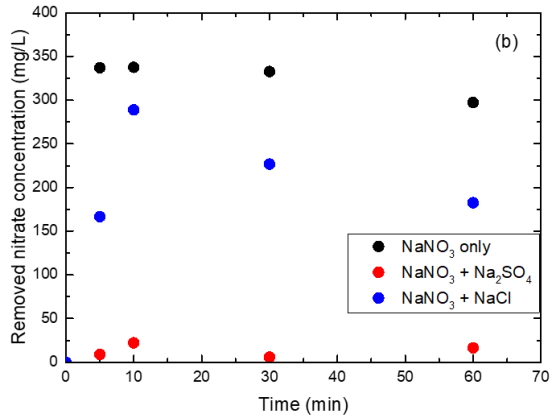
3.2 Column test

3.2.1 Performance evaluation by chemical composition of feed solution

In order to identify the individual effect of adsorption, a column experiment was conducted using various operating

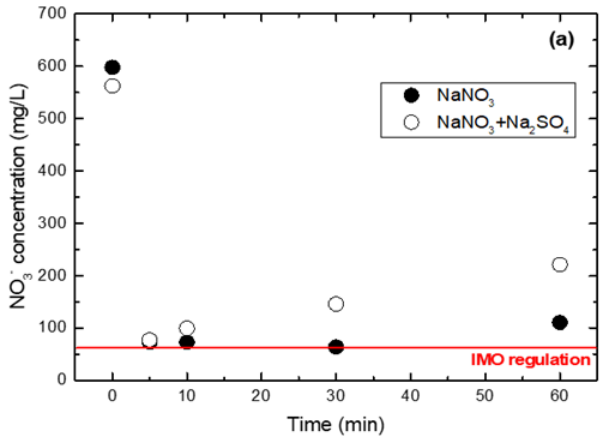


(a) A-62 MP resin

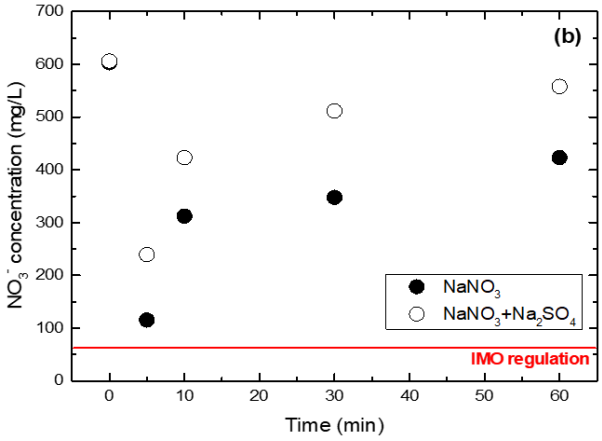


(b) MIEX resin

Fig. 3 Nitrate removal with various synthetic wastewater compositions by batch test of ion exchange resin



(a) A-62 MP resin



(b) MIEX resin

Fig. 4 Nitrate concentration of effluent flux after ion exchange resin column with various feed solution compositions

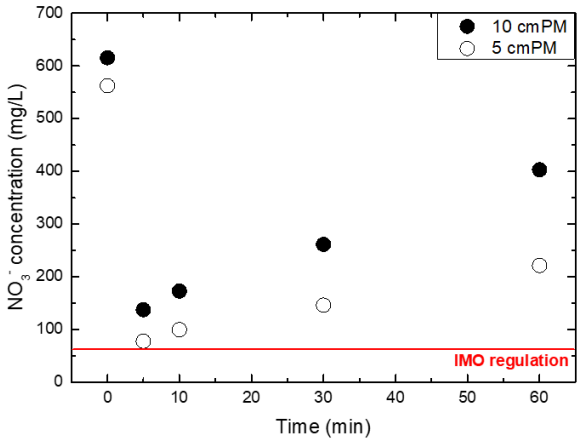


Fig. 5 Nitrate concentration of effluent flux after A-62 MP ion exchange resin column with various flow rates

conditions. We note that the effluent nitrate concentration for the sulfate + nitrate solution column experiment in Fig. 4 shows the same tendency as that displayed in Fig. 3.

This may be due to the higher affinity of MIEX resin towards sulfate ions than towards nitrate ions during the ion exchange processes according to the selectivity of MIEX resin. These results reveal that in the presence of sulfate and nitrate ions in wastewater, MIEX is not suitable to treat nitrate removal.

3.2.2 Performance evaluation by flow rate

To investigate the effect of flow rates on nitrate removal, experiments were performed where all conditions were identical except for the flow rate. Fig. 5 shows the nitrate removal amount as a function of the flow rate. The results show that the removal efficiency of nitrate increased when the flow rate was reduced. During one hour of operation, the nitrate concentrations of produced water were constantly increasing due to increasing saturated resin volume with high initial nitrate concentration.

3.2.3 Performance evaluation by bed volume (BV)

Fig. 6 shows the nitrate concentration of effluent solution with different bed volumes of A-62 MP resin (30% and 50%). Here the bed volume is equal to the volume of the column containing the packed ion exchange resin. The experiments were operated with flow rate of 5 cmPM.

As expected, the effluent nitrate concentration was lower with larger bed volume. With 50% bed volume, 93% initial and 86% average nitrate removal efficiencies were achieved during the 1 hour experiment. Moreover, the 50% bed volume experiment showed a mild decreasing trend of the removal rate (15.93%) as compared with the 30% bed volume experiment (35.59%).

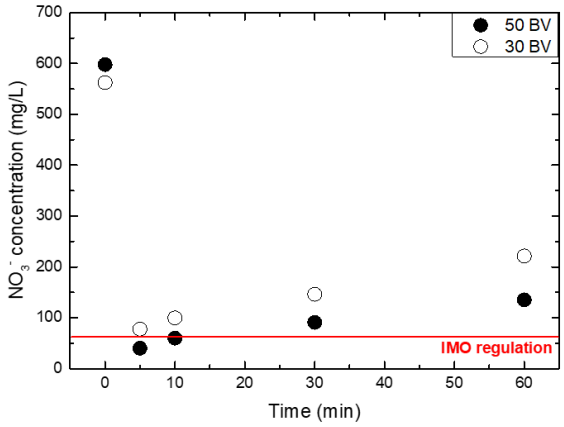


Fig. 6 Nitrate concentration of effluent flux after A-62 MP ion exchange resin column with various bed volumes

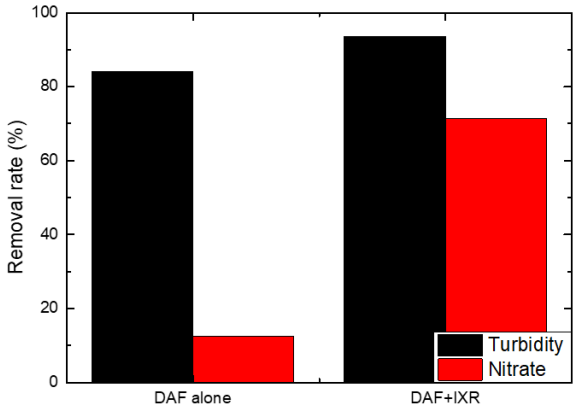


Fig. 7 Turbidity and nitrate removal rate by DAF alone and DAF+ion exchange process

3.3 Pilot test with dissolved air flotation (DAF) system

Fig. 7 shows the removal rate of turbidity and nitrate ion by pilot scale DAF and DAF+IXR process. It is revealed that DAF alone process effectively removed the turbidity material, however the removal efficiency of nitrate, ionic material, was significantly low. On the other hand, DAF with ion exchange resin process, the turbidity removal was also slightly increased compared to the DAF alone process, and the nitrate removal showed remarkably high performance, and it was confirmed that it is able to meet the IMO regulation about discharge water quality of scrubber wash water.

4. Conclusions

Ion exchange resin process is feasible to remove nitrate in high TDS wastewater such as wet scrubber wash water treatment during its ion selectivity. In this study, we investigate that ion exchange resins, A-62 MP and MIEX, can be used for nitrate removal from water. However, A-62 MP resin is more efficient in removing nitrate than MIEX with high TDS scrubber wastewater, especially wastewater including sulfate, because the nitrate selectivity for ion exchange was higher for A-62 MP than for MIEX resin.

This study also revealed that operating conditions such as flow rate and bed volume of ion exchange resin influence the nitrate removal performance resulting in the retention time of column. The ion exchange packed column system can effectively remove the nitrate ions from synthetic scrubber wastewater with more than 90% nitrate initial removal by optimization of operating conditions such as the flow rate and bed volume. Finally, our results imply that it is possible to meet the regulations of IMO scrubber wastewater discharge by pilot scale DAF with ion exchange resin process.

Acknowledgments

This research was supported by a grant (code 21CTAP-C152251-03) from Technology Advancement Research Program (TARP) funded by Ministry of Land, Infrastructure and Transport of Korea government and the project titled ‘Development of High Efficiency Scrubber for Simultaneous Reduction of Air Pollutants’, funded by the Ministry of Oceans and Fisheries, Korea.

References

Du, X., Ye, S. and Dong, D. (2019), “Rapid determination of nitrate in drinking water using ion-exchange-enhanced infrared spectroscopy”, *J. Food Process Eng.*, **42**(6), e13164. https://doi.org/10.1111/jfpe.13164.

Epsztein, R., Nir, O., Lahav, O. and Green, M. (2015), “Selective nitrate removal from groundwater using a hybrid nanofiltration–reverse osmosis filtration scheme”, *Chem. Eng. J.*, **279**, 372-378. https://doi.org/10.1016/j.cej.2015.05.010.

Fan, Y.V., Perry, S., Klemeš, J.J. and Lee, C.T. (2018), “A review on air emissions assessment: Transportation”, *J. Clean. Prod.*, **194**, 673-684. https://doi.org/10.1016/j.jclepro.2018.05.151.

Halff, A., Younes, L. and Boersma, T. (2019), “The likely implications of the new IMO standards on the shipping industry”, *Energy Policy*, **126**, 277-286. https://doi.org/10.1016/j.enpol.2018.11.033.

Isacs, L., Finnveden, G., Dahllöf, L., Håkansson, C., Petersson, L., Steen, B., Swanström, L. and Wikström, A. (2016), “Choosing a monetary value of greenhouse gases in assessment tools: A comprehensive review”, *J. Clean. Prod.*, **127**, 37-48. https://doi.org/10.1016/j.jclepro.2016.03.163.

Kamimura, A., Murata, K., Kawamoto, T. (2017), “An efficient and selective conversion of sorbitol in ionic liquids: Use of ion exchange resin as a solid acid catalyst”, *Tetrahedron Lett.*, **58**(37), 3616-3618. https://doi.org/10.1016/j.tetlet.2017.07.105.

Kim, A.R. and Seo, Y.J. (2019), “The reduction of SOx emissions in the shipping industry: The case of Korean companies”, *Mar. Policy*, **100**, 98-106. https://doi.org/10.1016/j.marpol.2018.11.024.

Li, K., Wu, M., Gu, X., Yuen, K.F. and Xiao, Y. (2020), “Determinants of ship operators’ options for compliance with IMO 2020”, *Transp. Res. D*, **86**, 102459. https://doi.org/10.1016/j.trd.2020.102459.

Lindstad, H.E. and Eskeland, G.S. (2016), “Environmental regulations in shipping: Policies leaning towards globalization of scrubbers deserve scrutiny”, *Transp. Res. D.*, **47**, 67-76. https://doi.org/10.1016/j.trd.2016.05.004.

Lytle, D.A., Sorg, T.J., Wang, L., Muhlen, C., Rahrig, M. and French, K. (2007), “Biological nitrification in a full-scale and pilot-scale iron removal drinking water treatment plant”, *J.*

Water Supply Res. T., **56**(2), 125-136. https://doi.org/10.2166/aqua.2007.092.

Maucieri, C., Barbera, A.C., Vymazal, J. and Borin, M. (2017), "A review on the main affecting factors of greenhouse gases emission in constructed wetlands", *Agric. For. Meteorol.*, **236**, 175-193. https://doi.org/10.1016/j.agrformet.2017.01.006.

Muhammad, A., Soares, A. and Jefferson, B. (2019), "The impact of background wastewater constituents on the selectivity and capacity of a hybrid ion exchange resin for phosphorus removal from wastewater", *Chemosphere*, **224**, 494-501. https://doi.org/10.1016/j.chemosphere.2019.01.085.

Nekouei, R.K., Pahlevani, F., Assefi, M., Maroufi, S. and Sahajwalla, V. (2019), "Selective isolation of heavy metals from spent electronic waste solution by macroporous ion-exchange resins", *J. Hazard. Mater.*, **371**, 389-396. https://doi.org/10.1016/j.jhazmat.2019.03.013.

Ni, P., Wang, X. and Li, H. (2020), "A review on regulations, current status, effects and reduction strategies of emissions for marine diesel engines", *Fuel*, **279**, 118477. https://doi.org/10.1016/j.fuel.2020.118477.

Panasiuk, I. and Turkina, L. (2015), "The evaluation of investments efficiency of SOx scrubber installation", *Transp. Res. D*, **40**, 87-96. https://doi.org/10.1016/j.trd.2015.08.004.

Reinoso, D.M. and Tonetto, G.M. (2018), "Bioadditives synthesis from selective glycerol esterification over acidic ion exchange resin as catalyst", *J. Environ. Chem. Eng.*, **6**(2), 3399-3407. https://doi.org/10.1016/j.jece.2018.05.027.

Rezvani, F., Sarrafzadeh, M.H., Ebrahimi, S. and Oh, H.M. (2019), "Nitrate removal from drinking water with a focus on biological methods: A review", *Environ. Sci. Pollut. Res.*, **26**(2), 1124-1141. https://doi.org/10.1007/s11356-017-9185-0.

Robichaud, A. (2020), "An overview of selected emerging outdoor airborne pollutants and air quality issues: The need to reduce uncertainty about environmental and human impacts", *J. Air Waste Manag. Assoc*., **70**(4), 341-378. https://doi.org/10.1080/10962247.2020.1723738.

Rubio, M.A., Lissi, E. and Villena G. (2002), "Nitrite in rain and dew in Santiago city, Chile. Its poissible impact on the early morning start of the photochemical smog", *Atmos. Environ*., **36**(2), 293-297. https://doi.org/10.1016/S1352-2310(01)00356-9.

Salima, C., Atmane, A., Marian, S., Souhila, R., Hayet, B. and Djoudi, M. (2018), "Treatment of produced water by induced air flotation: Effect of both TWEEN 80 and ethanol concentrations on the recovery of PAHs", *Nova Biotechnol. Chim.*, **17**(2), 181-192. https://doi.org/10.2478/nbec-2018-0019.

Seddiek, I.S. and Elgohary, M.M. (2014), "Eco-friendly selection of ship emissions reduction strategies with emphasis on SOx and NOx emissions", *Int. J. Nav. Archit. Ocean Eng.*, **6**(3), 737-748. https://doi.org/10.2478/IJNAOE-2013-0209.

Soyluoglu, M., Ersan, M.S., Ateia, M. and Karanfil, T. (2020), "Removal of bromide from natural waters: Bromide-selective vs. conventional ion exchange resins", *Chemosphere*, **238**, 124583. https://doi.org/10.1016/j.chemosphere.2019.124583.

Tan, L.L. and Li C.Z. (2000), "Formation of NOx and SOx precursors during the pyrolysis of coal and biomass. Part I. Effects of reactor configuration on the determined yields of HCN and NH_3 during pyrolysis", *Fuel*, **79**(15), 1883-1889. https://doi.org/10.1016/S0016-2361(00)00078-8.

Van, T.C., Ramirez, J., Rainey, T., Ristovski, Z. and Brown, R.J. (2019), "Global impacts of recent IMO regulations on marine fuel oil refining processes and ship emissions", *Transp. Res. D.*, **70**, 123-134. https://doi.org/10.1016/j.trd.2019.04.001.

Yang, Z.L., Zhang, D., Caglayan, O., Jenkinson, I.D., Bonsall, S., Wang, J., Huang, M. and Yan, X.P. (2012), "Selection of techniques for reducing shipping NOx and SOx emissions", *Transp. Res. D.*, **17**(6), 478-486. https://doi.org/10.1016/j.trd.2012.05.010.

Younker, J.M. and Walsh, M.E. (2014), "Bench-scale investigation of an integrated adsorption–coagulation–dissolved air flotation process for produced water treatment", *J. Environ. Chem. Eng.*, **2**(1), 692-697. https://doi.org/10.1016/j.jece.2013.11.009.

Zhang, X., Li, F. and Zhao, X. (2012), "Application of a magnetic resin (MIEX®) in wastewater reclamation for managed aquifer recharge", *Water Air Soil Pollut.*, **223**(8), 4687-4694. https://doi.org/10.1007/s11270-012-1225-2.

Zhou, J. and Wang, H. (2020), "Study on efficient removal of SOx and NOx from marine exhaust gas by wet scrubbing method using urea peroxide solution", *Chem. Eng. J.*, **390**, 124567. https://doi.org/10.1016/j.cej.2020.124567.

Zhou, Y., Shuang, C.D., Zhou, Q., Zhang, M.C., Li, P.H. and Li, A.M. (2012), "Preparation and application of a novel magnetic anion exchange resin for selective nitrate removal", *Chin. Chem. Lett.*, **23**(7), 813-816. https://doi.org/10.1016/j.cclet.2012.05.010.

YP